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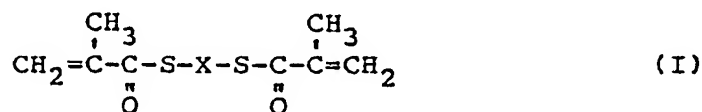
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(54) Thiolcarboxylic acid esters.

(57) Thiolcarboxylic acid esters represented by the general formula



wherein X represents $-\text{CH}_2\text{CH}_2-$, $+\text{CH}_2\text{CH}_2\text{O}+$, $+\text{nCH}_2\text{CH}_2-$, $+\text{CH}_2\text{CH}_2\text{S}+$, $+\text{mCH}_2\text{CH}_2-$, or



and n and m represent an integer of 1 to 3.

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THIOLCARBOXYLIC ACID ESTERS

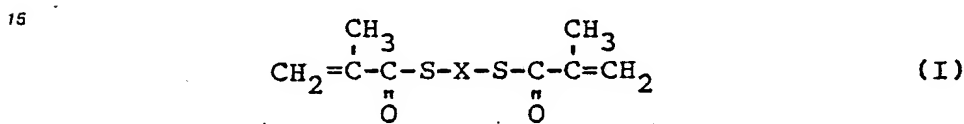
This invention relates to novel thiolcarboxylic acid esters useful as a material for optical plastics.

In recent years, transparent synthetic resins having a high refractive index have found increasing applications as optical plastic materials replacing inorganic optical materials because of their light weight and good impact strength, moldability or processability and dyeability.

5. A diethylene glycol bis-allyl carbonate resin as one example of conventional optical plastic materials has a refractive index of as low as 1.49 to 1.50. Hence, an eyeglass lens, for example, formed from this resin has the defect of being large in the thickness of both its center and edge as compared with inorganic optical lenses.

10 It is an object of this invention therefore to remedy the defects of conventional optical plastic materials, and to provide monomers which can give resins having a high refractive index and excellent transparency useful as an optical plastic material.

The present inventors, after conducting extensive work, have found that the above object is achieved by a compound (monomer) represented by the general formula



20 wherein X represents $-\text{CH}_2\text{CH}_2-$, $\text{CH}_2\text{CH}_2\text{O}$, $\text{CH}_2\text{CH}_2\text{CH}_2-$, $\text{CH}_2\text{CH}_2\text{S}$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$, or



and n and m represent an integer of 1 to 3.

Thus, according to this invention, the following eight compounds are provided.

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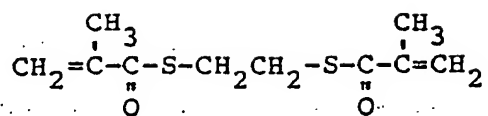
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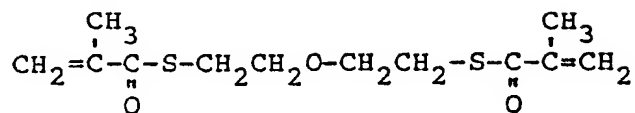
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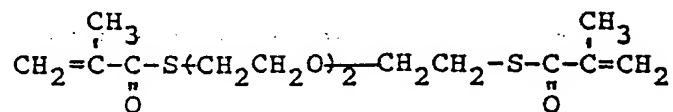
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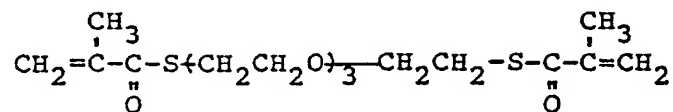
Compound (2):



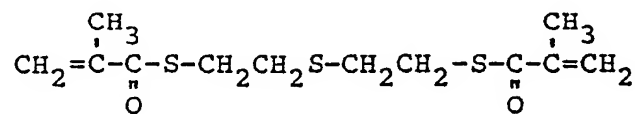
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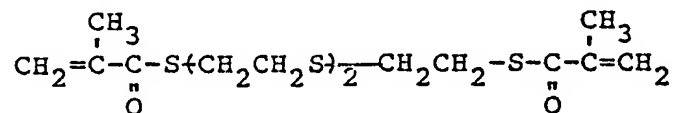
Compound (4):



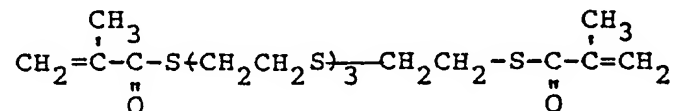
Compound (5):



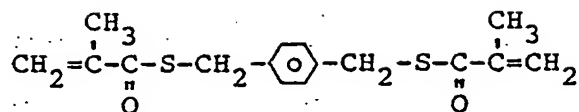
Compound (6):



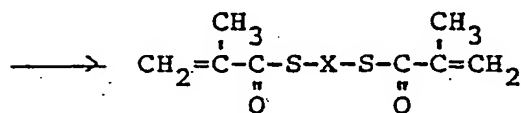
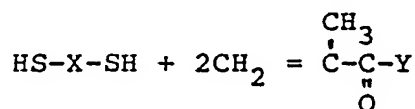
Compound (7):



Compound (8):



Compounds (1) to (8) in accordance with this invention can be produced by reacting a dithiol derivative with a methacrylic acid derivative in accordance with the following formula.



In the formula, X is as defined above, and Y represents Cl, Br, OH, or an alkoxy group having 1 to 4 carbon atoms.

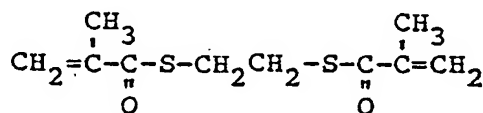
By polymerizing the novel thiocarboxylic acid esters (1) to (8) represented by general formula (I) or copolymerizing them together with various compounds having olefinic double bonds, polymers or oligomers can be obtained. The polymers have a high refractive index and excellent transparency. In addition, since they are three-dimensionally crosslinked resins, they have good processability characteristics such as machinability and grindability, and are suitable as optical plastics.

The present invention will be specifically described with reference to the following Examples and the accompanying drawings.

In the accompanying drawings, Figures 1, 4, 7, 10 and 13 are infrared absorption spectral charts of compounds (1), (2), (3), (5) and (8) respectively; Figures 2, 5, 8, 11 and 14 are ¹H-NMR spectral charts of compounds (1), (2), (3), (5) and (8) respectively; and Figures 3, 6, 9, 12 and 15 are ¹³C-NMR spectral charts of compounds (1), (2), (3), (5) and (8).

EXAMPLE 1

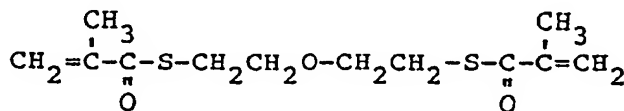
A 2000 ml glass flask equipped with a stirrer, a thermometer, a condenser and dropping funnels was charged with 5.36 g of trioctylmethyl ammonium chloride, 0.31 g of methoquinone and 480 g of chloroform. While the temperature of the inside of the flask was maintained at less than 10 °C, a separately prepared mixture of 25.0 g of 1,2-dimercaptoethane and 700.8 g of a 7.5 % by weight aqueous solution of potassium hydroxide and 66.6 g of methacryloyl chloride were added dropwise over 20 minutes through separate dropping funnels. After the addition, the mixture was further stirred at the same temperature for 15 minutes, and the reaction solution was then separated into two layers. The chloroform layer was washed with a 5 % by weight aqueous solution of potassium hydroxide and then with water, and dried over anhydrous sodium sulfate. Chloroform was evaporated to give 52.6 g (yield 86.1 %) of compound (1) of the following formula.



The product was purified by distillation under reduced pressure, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1. Its infrared absorption spectrum is shown in Figure 1; its ¹H-NMR spectrum, in Figure 2; and its ¹³C-NMR spectrum, in Figure 3.

EXAMPLE 2

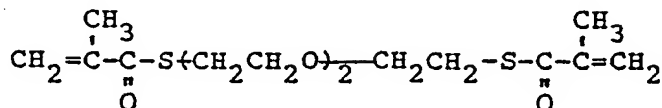
By the same method as in Example 1, compound (2) of the following formula was prepared in a yield of 90.2 % from 2-mercaptoethyl ether and methacryloyl chloride.



The product was purified by distillation under reduced pressure, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1. Its infrared absorption spectrum is shown in Figure 4; its ¹H-NMR spectrum, in Figure 5; and its ¹³C-NMR spectrum, in Figure 6.

EXAMPLE 3

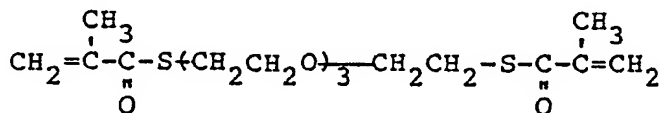
By the same method as in Example 1, compound (3) of the following formula was prepared in a yield of 89.3 % from 1,2-bis-(2-mercaptoethoxy)ethane and methacryloyl chloride.



The product was purified by silica gel column chromatography, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1. Its infrared absorption spectrum is shown in Figure 7; its ¹H-NMR spectrum, in Figure 8; and its ¹³C-NMR spectrum, in Figure 9.

EXAMPLE 4

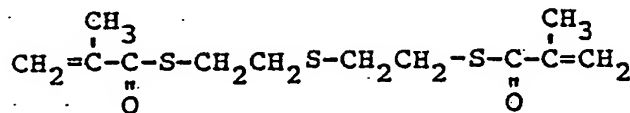
By the same method as in Example 1, compound (4) of the following formula was prepared in a yield of 84.0 % from bis-2-(2-mercaptoethoxy)ethyl ether and methacryloyl chloride.



The product was purified by silica gel column chromatography, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1.

EXAMPLE 5

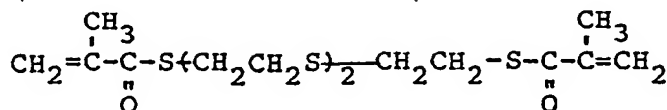
By the same method as in Example 1, compound (5) of the following formula was prepared in a yield of 93.1 % from 2-mercaptoethyl sulfide and methacryloyl chloride.



The product was purified by distillation under reduced pressure, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1. Its infrared absorption spectrum is shown in Figure 10; its ¹H-NMR spectrum, in Figure 11; and its ¹³C-NMR spectrum, in Figure 12.

EXAMPLE 6

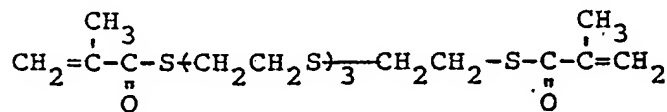
By the same method as in Example 1, compound (6) of the following formula was prepared in a yield of 88.7 % from 1,2-bis-(2-mercaptoethylthio)ethane and methacryloyl chloride.



The product was purified by silica gel column chromatography, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1.

EXAMPLE 7

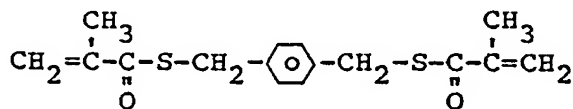
By the same method as in Example 1, compound (7) of the following formula was prepared in a yield of 82.5 % from bis-2-(2-mercaptoethylthio)ethyl sulfide and methacryloyl chloride.



The product was purified by silica gel column chromatography, and its structure was determined by elemental analysis, mass analysis, and infrared absorption spectroscopy. The results are shown in Table 1.

EXAMPLE 8

By the same method as in Example 1, compound (8) of the following formula was prepared in a yield of 73.6 % from 1,4-bis-mercaptomethylbenzene and methacryloyl chloride.



The product was purified by recrystallization, and its structure was determined by elemental analysis,

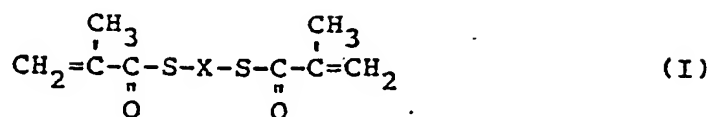
mass analysis and infrared absorption spectroscopy. The results are shown in Table 1. Its infrared absorption spectrum is shown in Figure 13; its ^1H -NMR spectrum, in Figure 14; and its ^{13}C -NMR spectrum, in Figure 15.

Table 1

Compound	Properties (boiling point)	Elemental analysis (%)		Mass analysis (M^+)	Character- istic infrared absorption (cm^{-1})
		Calcu- lated	Found		
(1)	Colorless trans- parent liquid (124-125°C/1.1mmHg)	C: 52.14 H: 6.13 S: 27.84	C: 52.39 H: 6.09 S: 27.57	230	$\nu \text{C}=\text{O}$ 1660
(2)	Colorless trans- parent liquid (133-134°C/1.0mmHg)	C: 52.53 H: 6.61 S: 23.37	C: 52.36 H: 6.72 S: 23.49	274	$\nu \text{C}=\text{O}$ 1660
(3)	Colorless trans- parent liquid	C: 52.80 H: 6.96 S: 20.14	C: 53.51 H: 7.04 S: 20.12	318	$\nu \text{C}=\text{O}$ 1660
(4)	Colorless trans- parent liquid	C: 53.01 H: 7.23 S: 17.69	C: 52.14 H: 7.09 S: 17.51	362	$\nu \text{C}=\text{O}$ 1660
(5)	Colorless trans- parent liquid (170-171°C/1.0mmHg)	C: 49.62 H: 6.25 S: 33.11	C: 49.40 H: 6.38 S: 33.37	290	$\nu \text{C}=\text{O}$ 1660
(6)	Colorless trans- parent liquid	C: 47.97 H: 6.33 S: 36.58	C: 47.20 H: 6.46 S: 36.99	350	$\nu \text{C}=\text{O}$ 1660
(7)	Colorless trans- parent liquid	C: 46.79 H: 6.38 S: 39.03	C: 47.00 H: 6.49 S: 38.85	410	$\nu \text{C}=\text{O}$ 1660
(8)	White crystals (melting point: 64-65°C)	C: 62.71 H: 5.92 S: 20.93	C: 62.63 H: 5.75 S: 21.01	306	$\nu \text{C}=\text{O}$ 1655

Claims

1. A thiolcarboxylic acid ester represented by the general formula

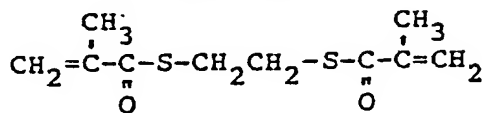


wherein X represents $-\text{CH}_2\text{CH}_2-$, $+\text{CH}_2\text{CH}_2\text{O}+$, $+\text{CH}_2\text{CH}_2\text{CH}_2-$, $+\text{CH}_2\text{CH}_2\text{S}+$, $+\text{CH}_2\text{CH}_2\text{CH}_2-$, or

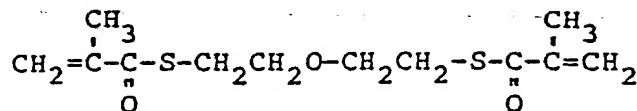


and n and m represent an integer of 1 to 3

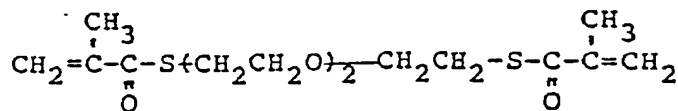
2. A compound of the formula:



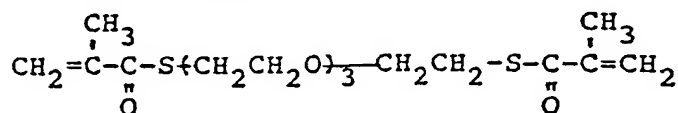
3. A compound of the formula:



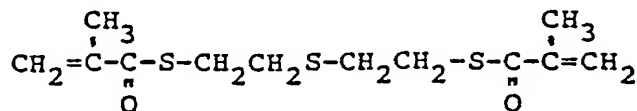
4. A compound of the formula:



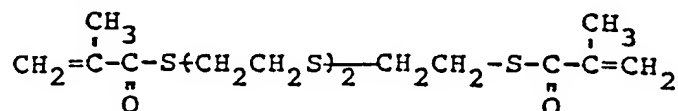
5. A compound of the formula:



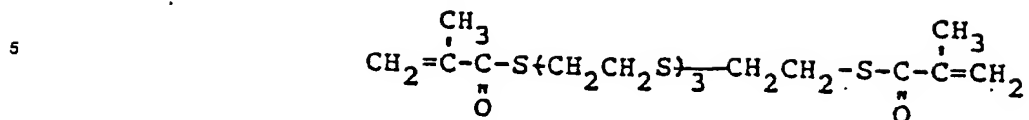
6. A compound of the formula:



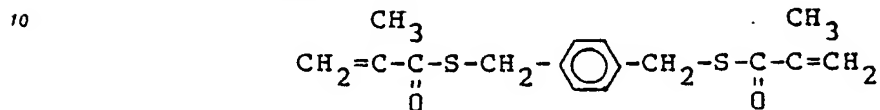
7. A compound of the formula:



A compound of the formula:



A compound of the formula:



15 10. A polymer of a thiolcarboxylic acid ester as claimed in any one of the preceding claims.

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FIG. 1

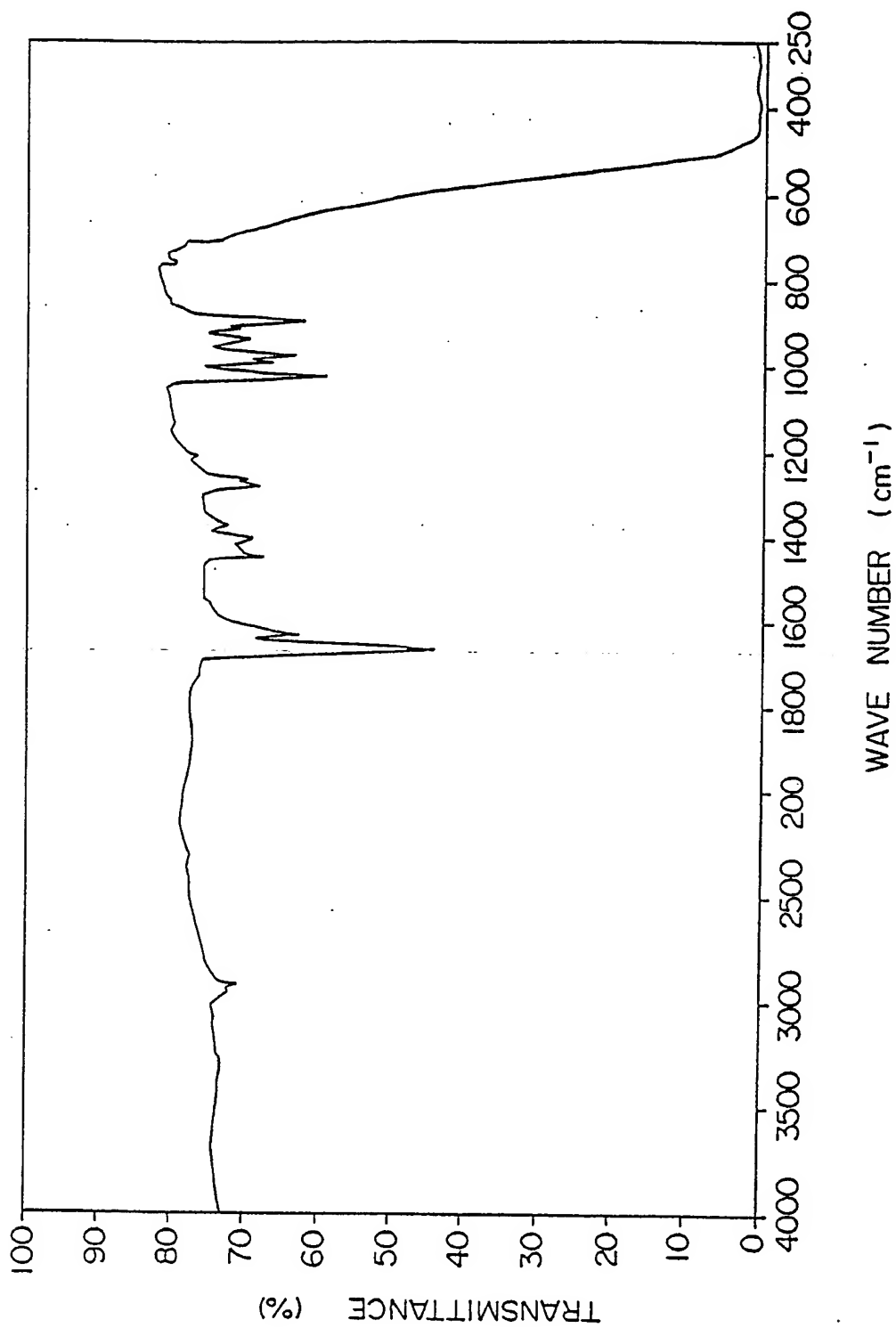


FIG. 2

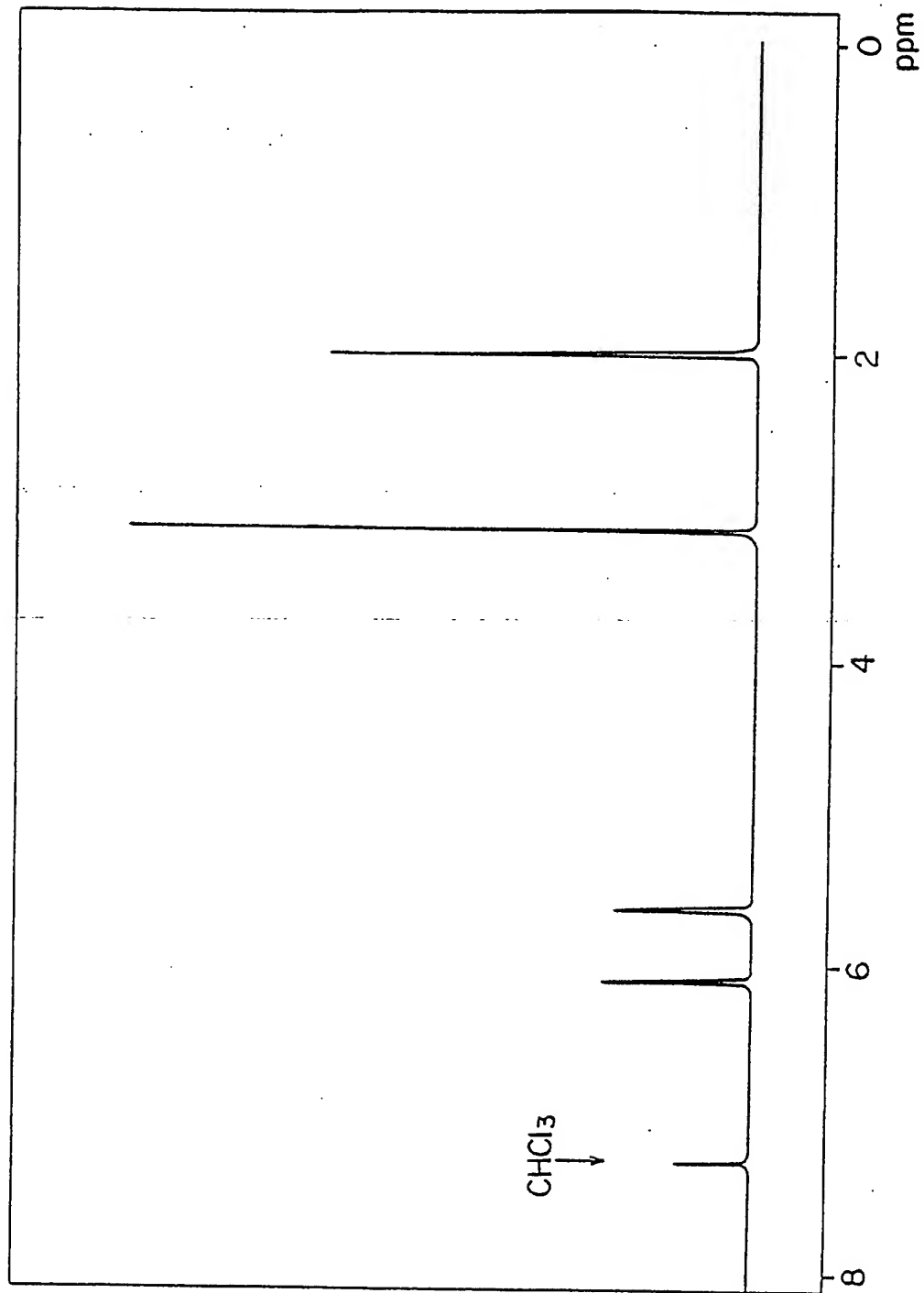


FIG. 3

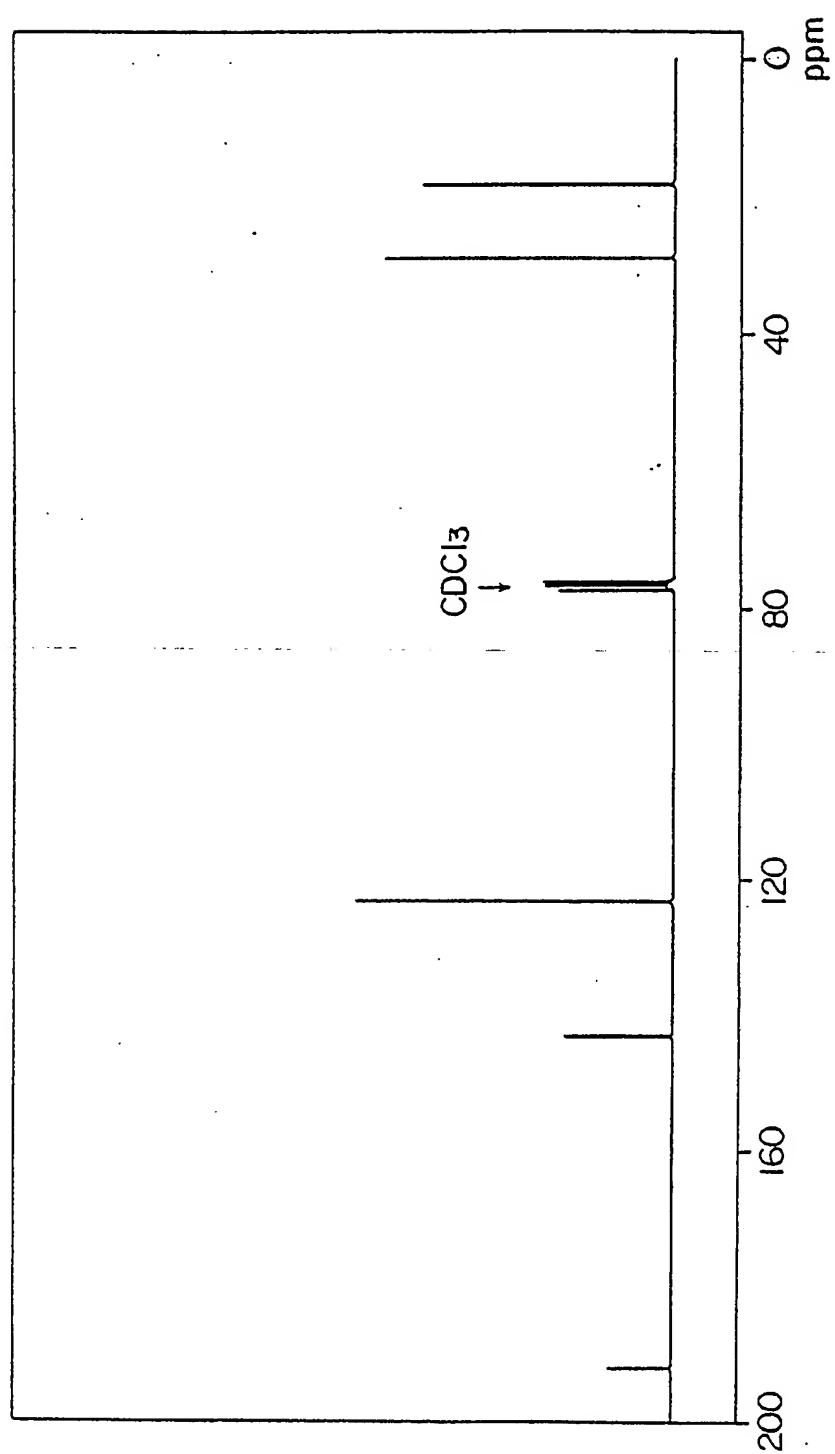


FIG. 4

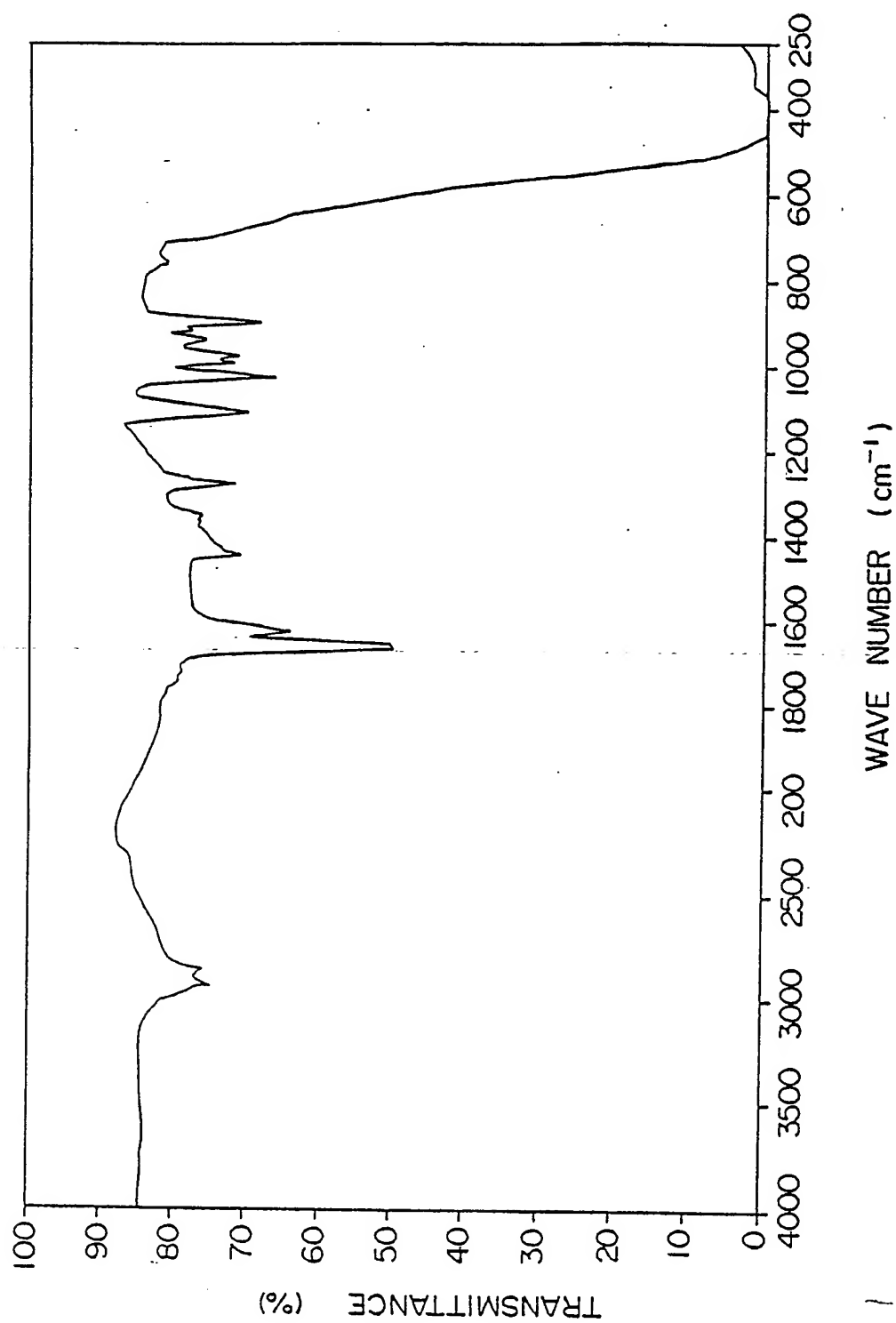


FIG. 5

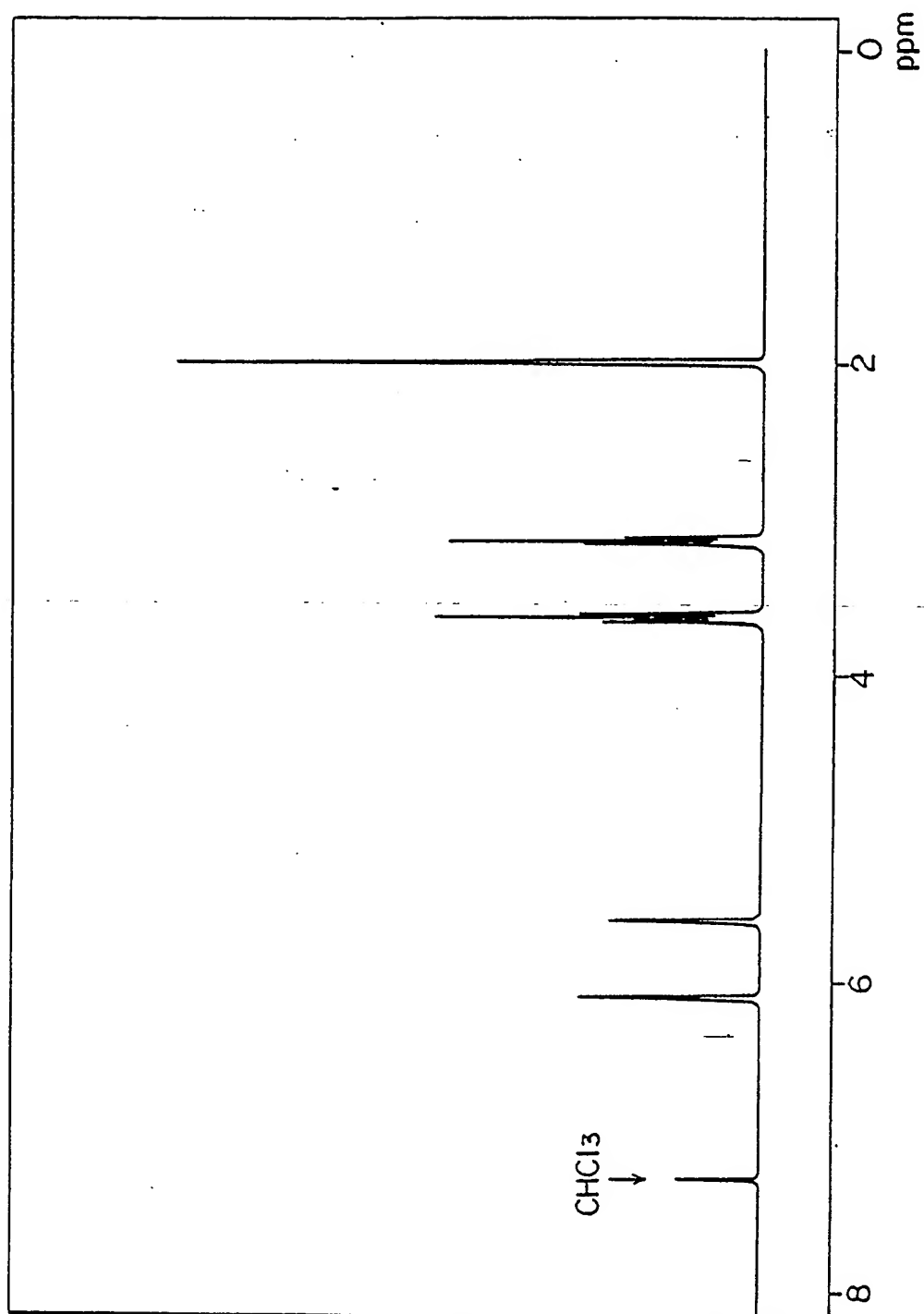


FIG. 6

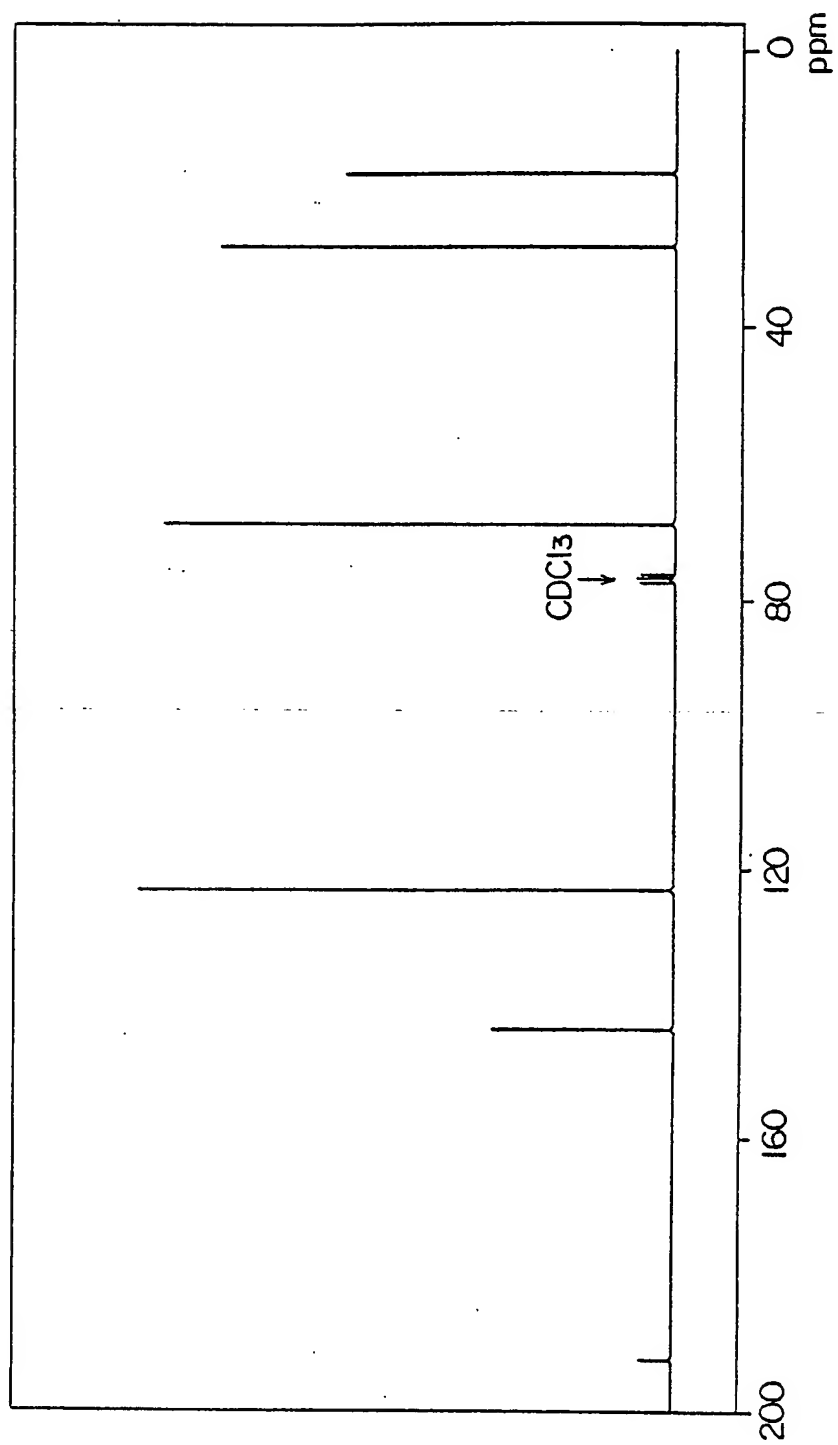


FIG. 7

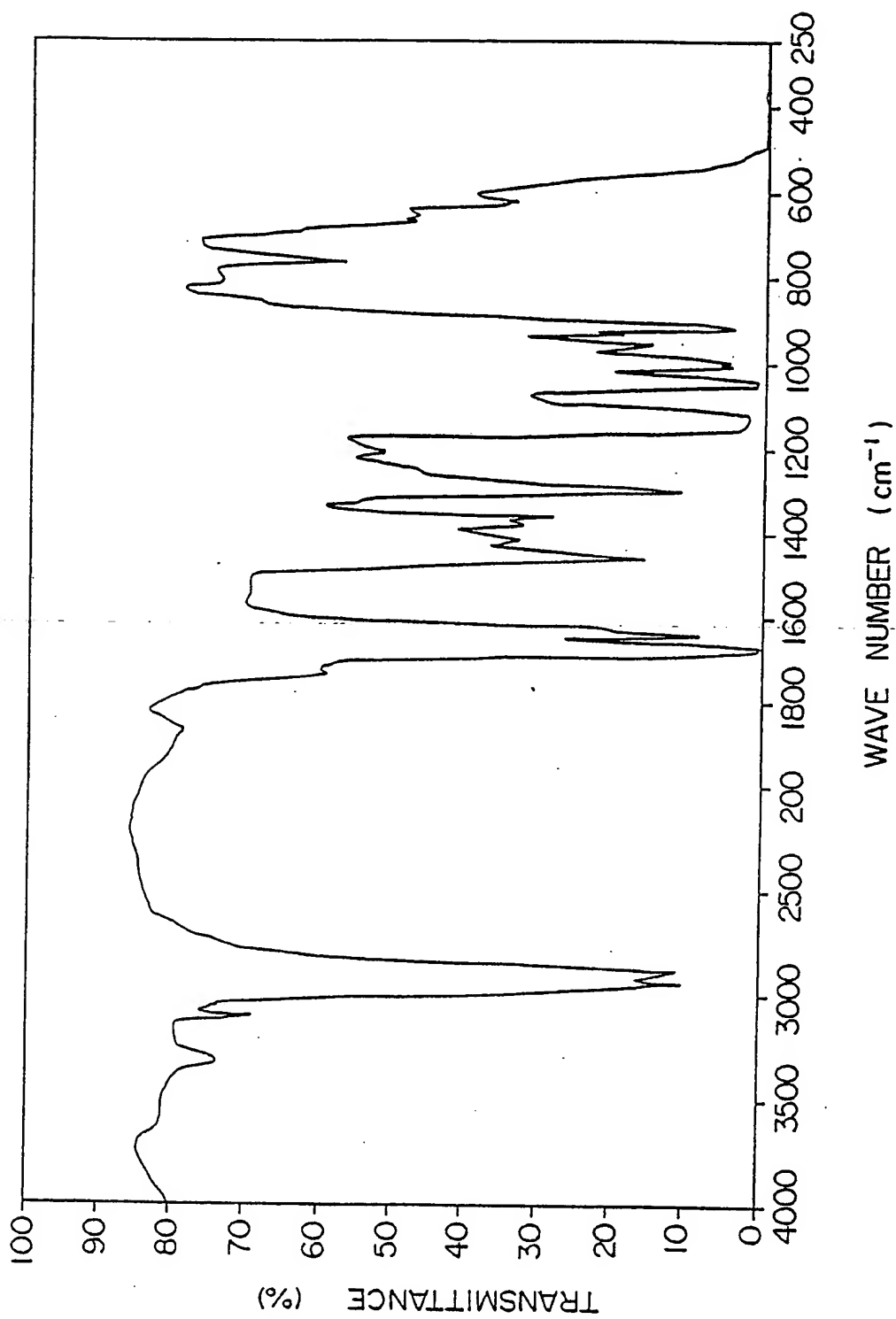


FIG. 8

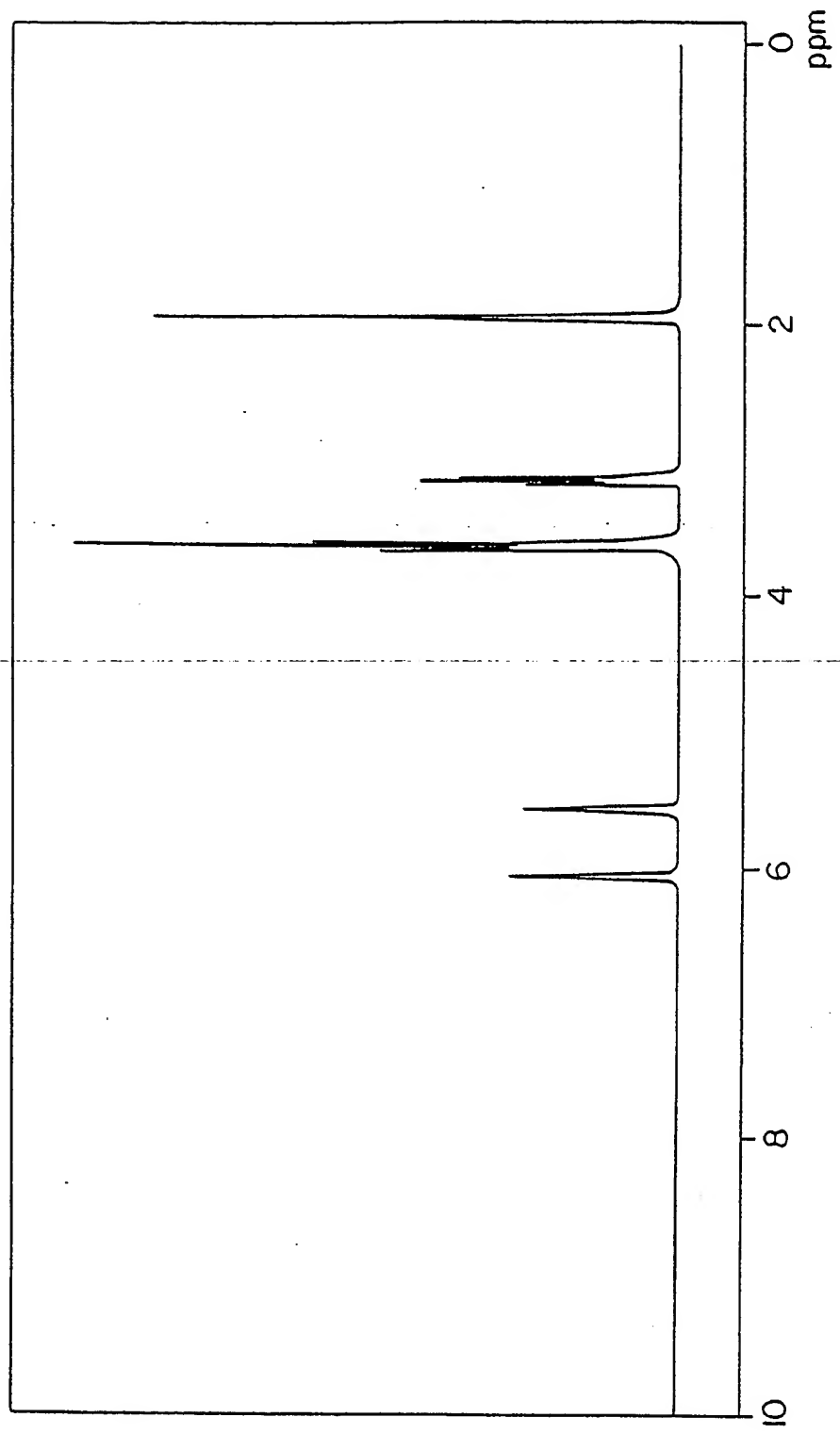


FIG. 9

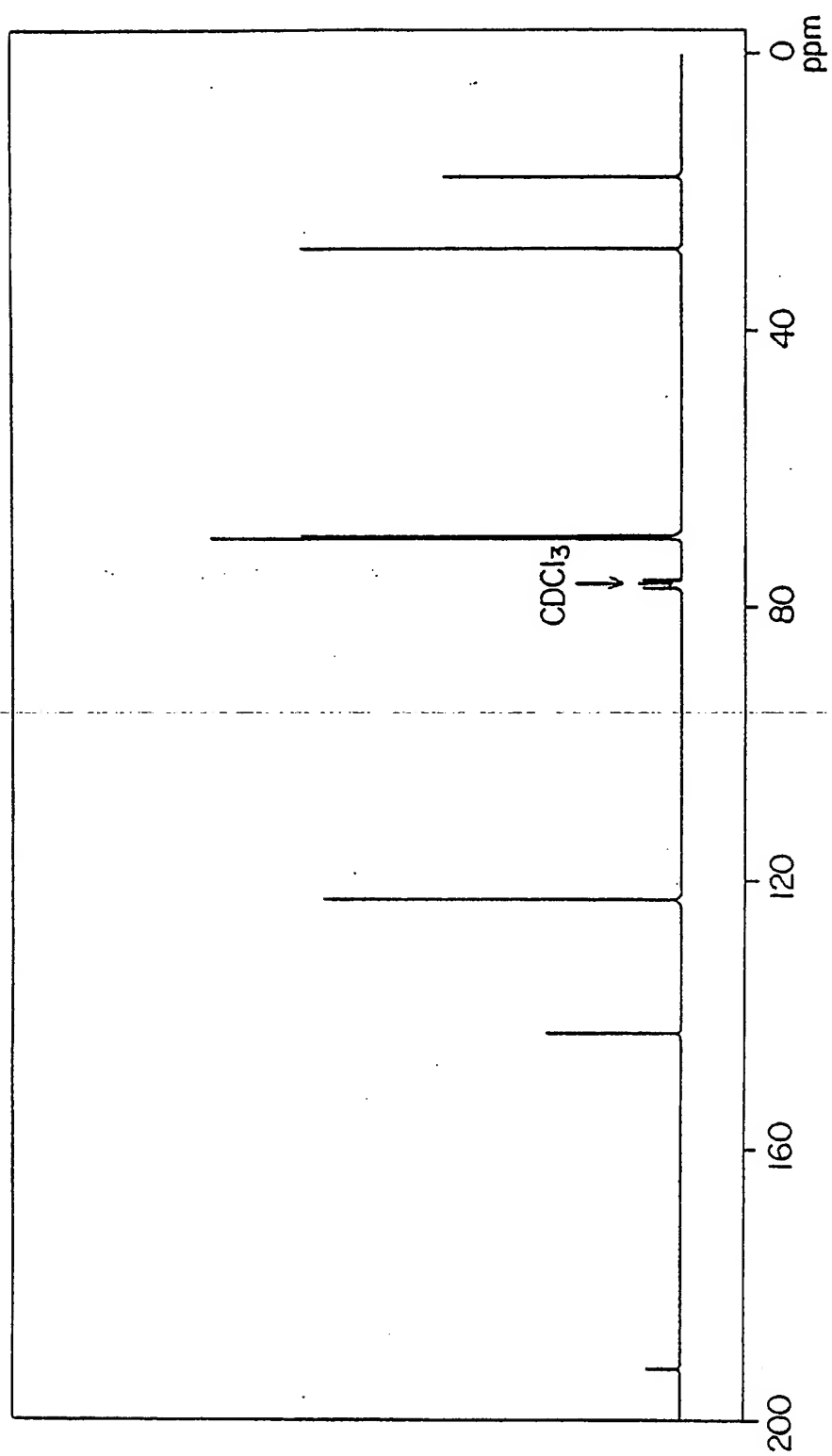


FIG. 10

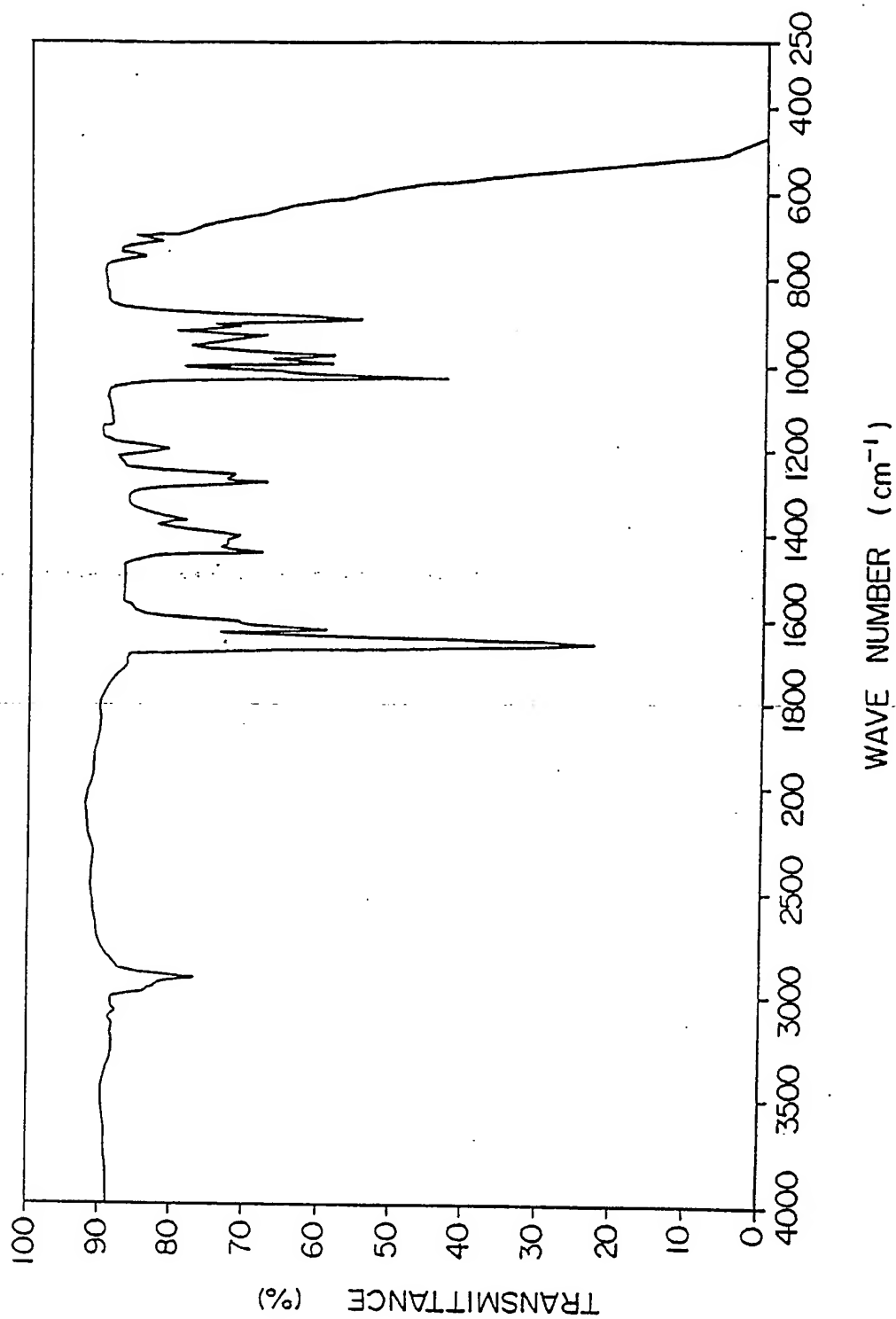


FIG. II

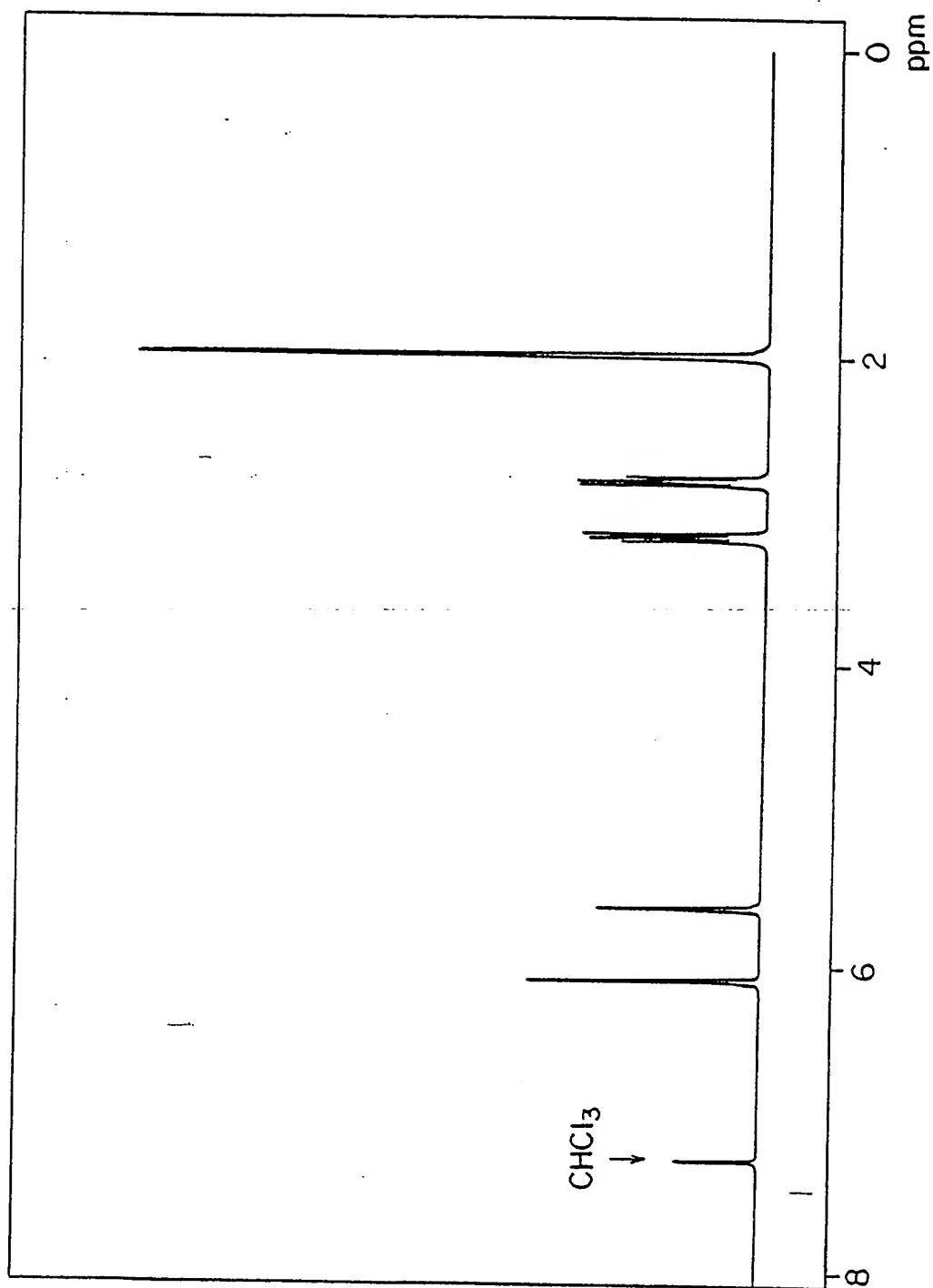


FIG. 12

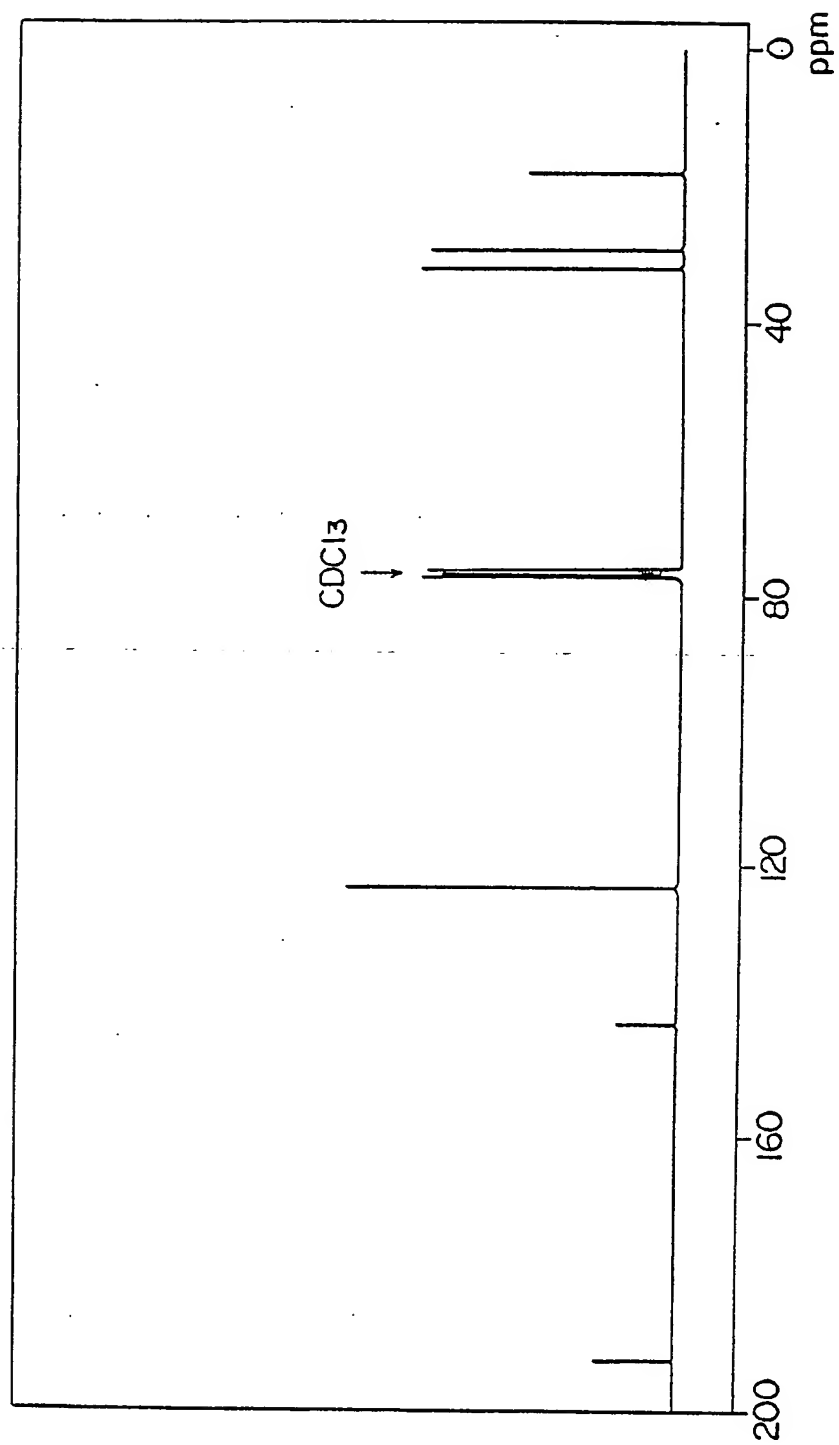


FIG. 13

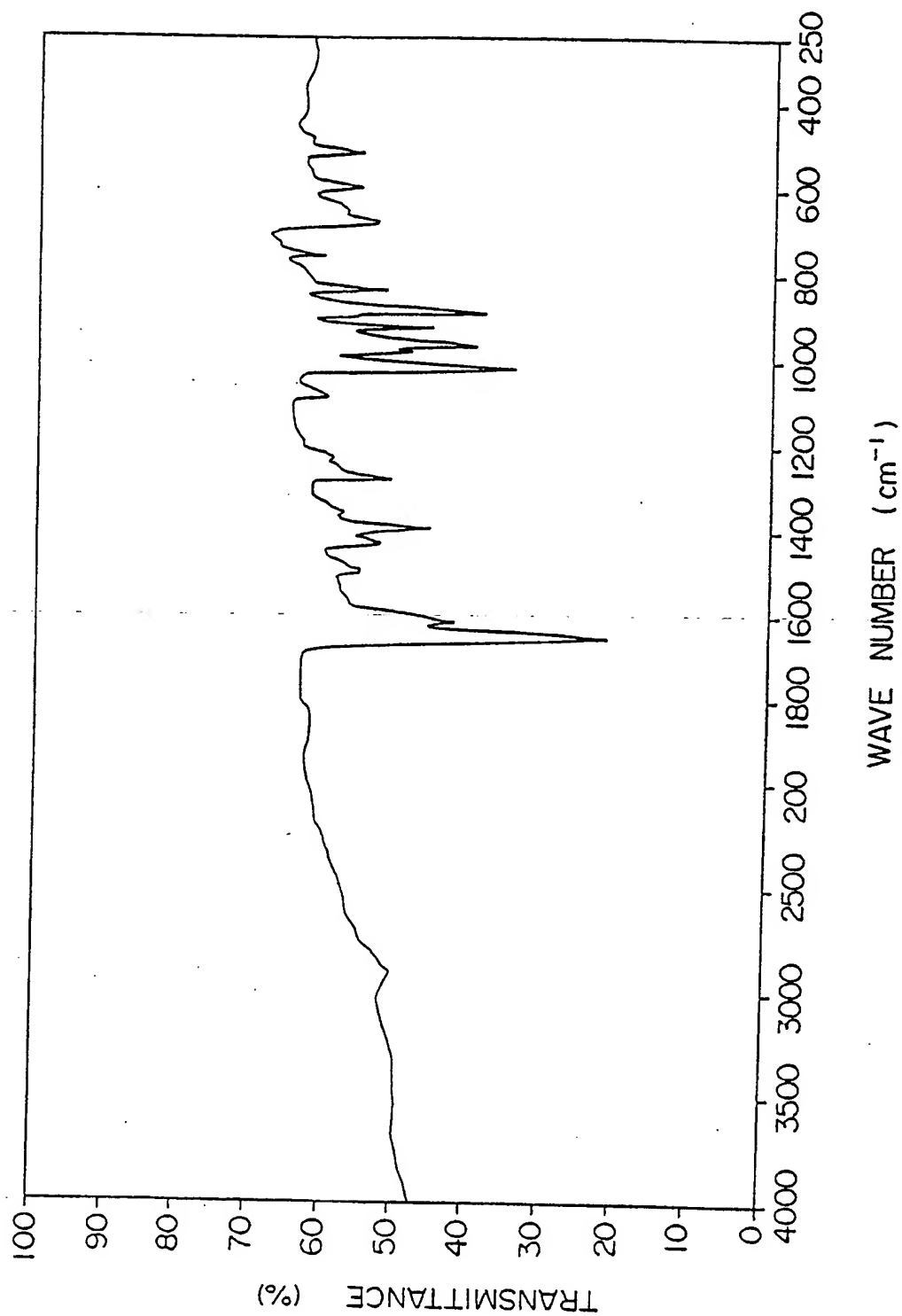


FIG. 14

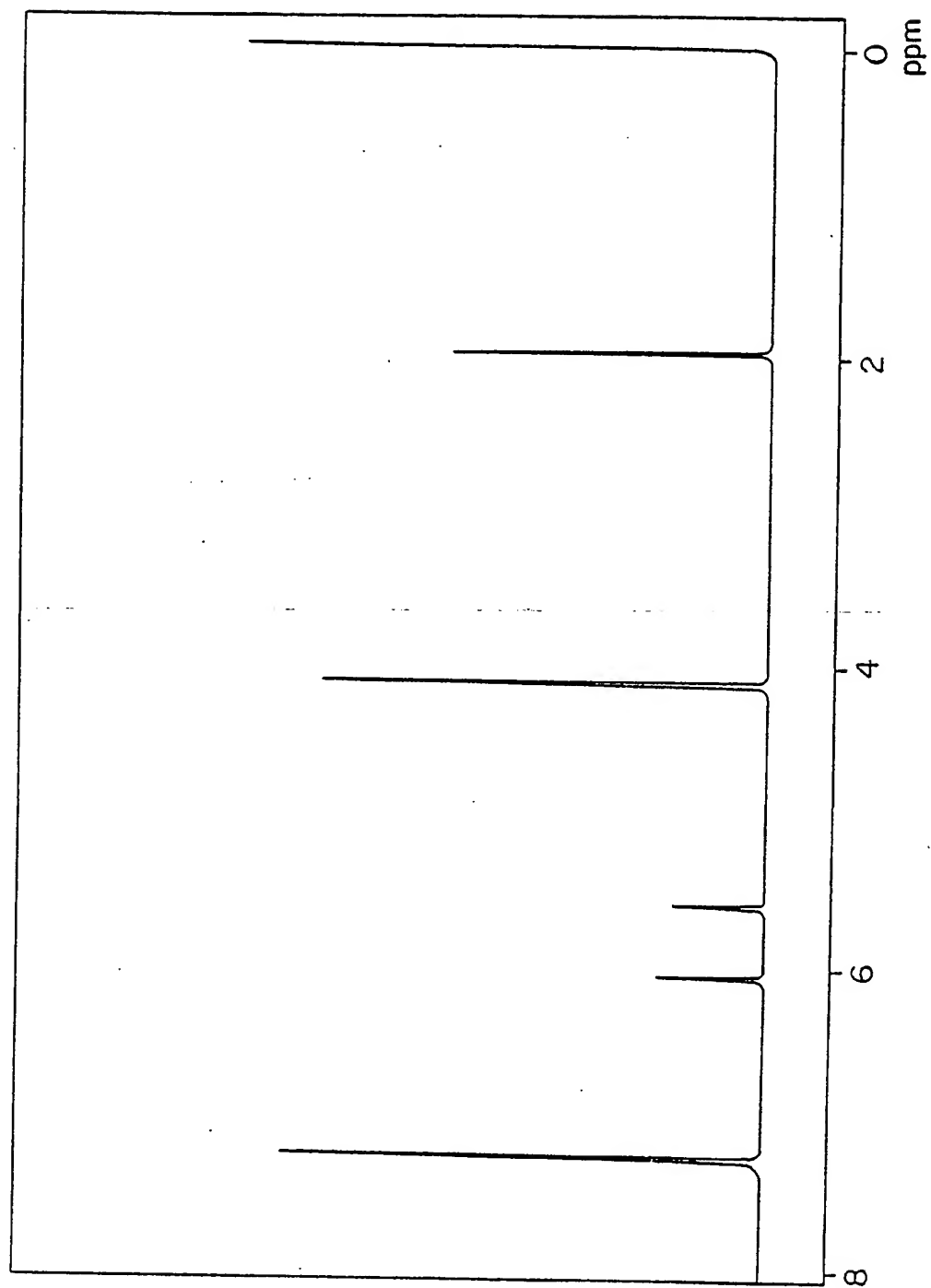
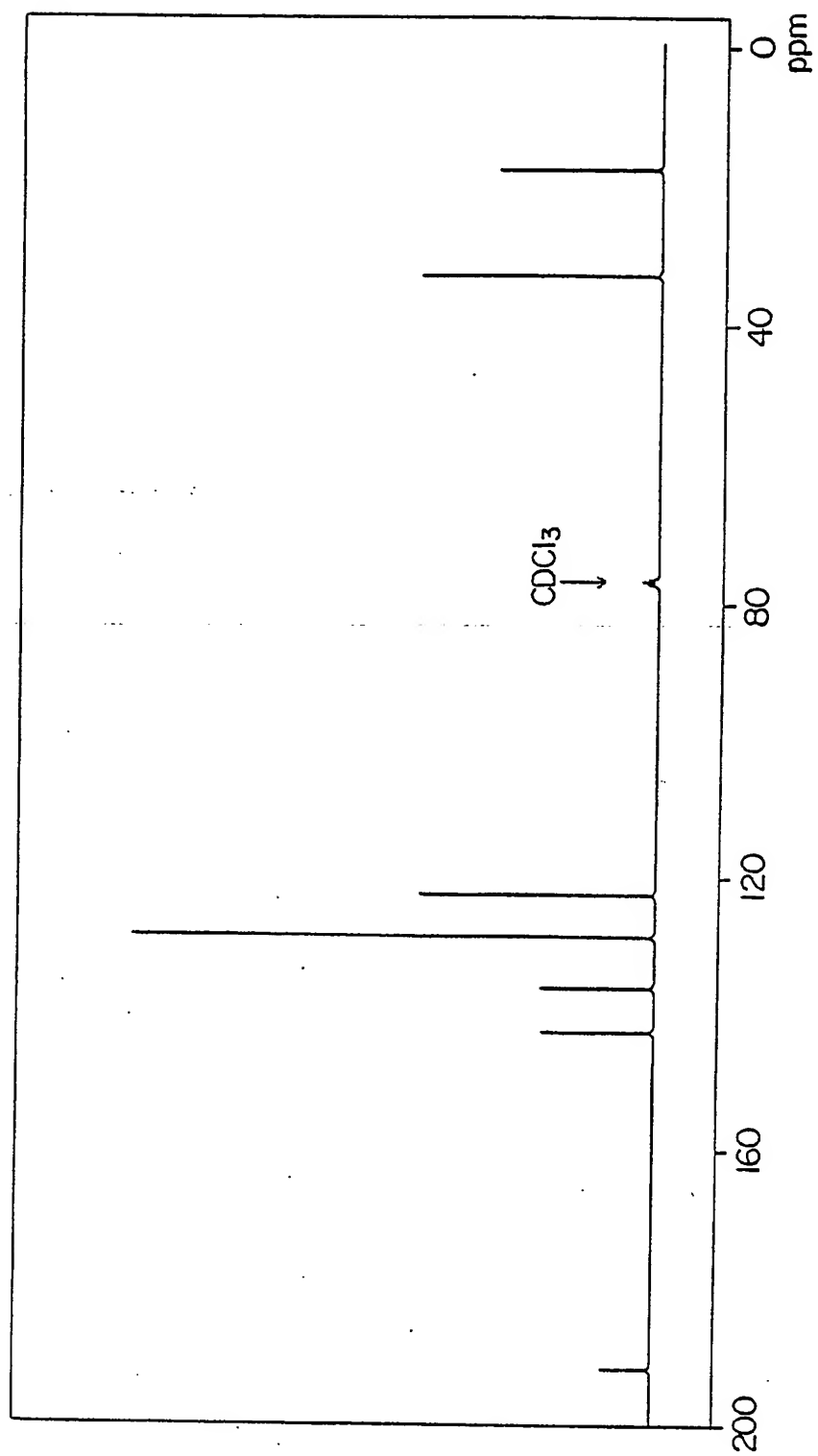


FIG. 15





EP 87 31 1203

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB-A-2 093 843 (EASTMAN KODAK CO.) ---		C 07 C 153/11
A	US-A-4 606 864 (WARREN) -----		C 08 F 120/38
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 07 C 153/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10-03-1988	Examiner VAN GEYT J.J.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			